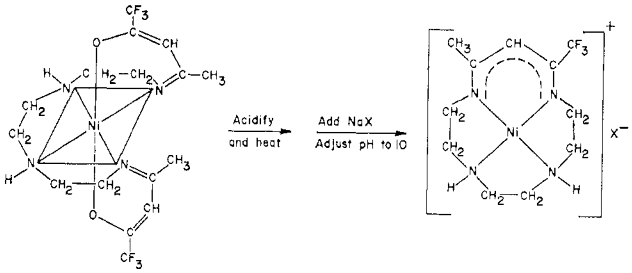

Figure 2.—Rearrangement of Ni(BTAT) to Ni(TAT)X. (The *trans* isomer of Ni(BTAT) has been shown arbitrarily.)

upon the asymmetry of the coordinated secondary amines. We have not pursued this aspect of the problem other than to note that two forms of Ni(AT)Br, one yellow and one red, could be isolated. These may be isomers or simply different hydrates. A thorough study of the isomer possibilities is now underway.[22]

Attempts to prepare the cyclic ligands in the absence of nickel(II) ions have so far been unsuccessful. It is therefore inferred that the condensation is controlled by metal ion template effects. This seems particularly reasonable in the synthesis of Ni(TAT)X complexes *via* rearrangement of Ni(BTAT). In this reaction, shown in Figure 2, the nickel(II) ion may be required to hold the ligand in a position such that acid-catalyzed self-condensation of the sexadentate Schiff base can occur with loss of 1 mol of trifluoroacetylacetone. Regardless of which of the three reported methods is used, cyclization seems to be favored, even when it requires condensation at a carbonyl oxygen adjacent to a normally deactivating $-CF_3$ group.

In view of the foregoing discussion, the new compounds are unique in two ways: (1) the Ni(TAT)X derivatives provide the first examples of chelate formation involving condensation at a carbonyl oxygen adjacent to a trifluoromethyl group; and (2) members of the Ni(TAT)X and Ni(AT)X series are the first macrocyclic metal complexes to be synthesized by condensation of both oxygen atoms of a β-diketone with a polyamine.

In addition, the uninegative nature of the two ligands, resulting in partial delocalization of the six-membered chelate ring within the macrocycles, is most important and serves to distinguish these complexes from the tetraazadienes of Curtis[23] (neutral ligands), and the tetraazaannulens of Jäger[24] (ligands of double negative charge) which are models of the well known phthalocyanines and porphyrins. The cyclization reaction reported here may ultimately provide the first simple route to metal complexes containing macrocyclic ligands of uninegative charge, which should serve as models for the corrin ring. The scope and general applicability of these reactions are currently being investigated.

Acknowledgment.—The authors wish to thank Dr. Daryle H. Busch for helpful discussions during the course of this work.

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(22) W. Elfring and N. J. Rose, private communication, University of Washington, 1969.

(23) N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

(24) E. G. Jäger, *Z. Anorg. Allgem. Chem.*, **364**, 177 (1969), and references therein.

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Iodonium Salts of Complex Anions. II.[1] Pyrolytic Autoarylation Reactions of Diphenyliodonium Bis(N-cyanodithiocarbimato)nickel(II)

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Received November 6, 1969

Diphenyliodonium bis(N-cyanodithiocarbimato)nickel(II) has been prepared and its solid-state thermal autoarylation studied. The diphenyliodonium cation phenylates the complex anion; attack occurs on the two sulfur atoms of the same ligand. This has been verified by the isolation and identification of N-cyanodiphenyldithiocarbimate, $(C_6H_5S)_2C{=}NC{\equiv}N$. As a result of the phenylation the configuration about nickel changes from planar to octahedral, giving a polymeric species.

Introduction

The usefulness of the diphenyliodonium cation (dpi) for precipitating complex anions in pure form and good yield from aqueous solution has been demonstrated. Isolation and reactions of dpi salts of the binegative anions tetrachloroplatinate(II)[2] and bis(dithiooxalato)platinate(II) and -palladate(II)[1] have been reported. As part of our investigation on ligand reactions of dpi salts of complex anions, we have conducted studies employing the diprotic ligand N-cyanodithiocarbimate (cdc). The preparation and characterization of tetramethylammonium[3] and tetrapropylammonium[4] salts of the anion bis(N-cyanodithiocarbimato)nickel(II) have been reported recently.

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(1) Part I: G. E. Hunter and R. A. Krause, *Inorg. Chem.*, **9**, 537 (1970).

(2) R. A. Krause, *ibid.*, **4**, 1227 (1965).

(3) F. A. Cotton and J. A. McCleverty, *ibid.*, **6**, 229 (1967).

(4) (a) J. P. Fackler, Jr., and D. Coucouvanis, *Chem. Commun.*, 556 (1965); (b) J. P. Fackler, Jr., and D. Coucouvanis, *J. Am. Chem. Soc.*, **88**, 3913 (1966).

In this paper we wish to report the isolation and especially the results of the pyrolysis reaction of diphenyliodonium bis(N-cyanodithiocarbimato)nickel(II), $(dpi)_2[Ni(cdc)_2]$ (I).

Experimental Section

Chemicals.—Cyanamide (50% aqueous solution) was obtained from Aldrich Chemical Co., Milwaukee, Wis., phenyldithiobenzene from Eastman Organic Chemicals, Rochester, N. Y., and iodobenzene from Matheson Coleman and Bell, East Rutherford, N. J. All other chemicals were of reagent grade and were used as received.

Diphenyliodonium Chloride.—This was prepared by following the procedure recorded by Beringer, *et al.*[5] The product melting at 228° dec was used.

Dipotassium N-Cyanodithiocarbimate Solution (Potassium Cyanodithioimidocarbonate).—Each time about 60 ml of yellow or orange solution containing the N-cyanodithiocarbimate anion was obtained following the directions of Fackler and Coucouvanis[4b] employing 8.4 ml of 50% aqueous solution of cyanamide.

Tetramethylammonium Bis(N-cyanodithiocarbimato)nickel(II), $((CH_3)_4N)_2[Ni(cdc)_2]$.—This compound was prepared using aqueous solutions of $Ni(ClO_4)_2 \cdot 6H_2O$ (3.65 g in 20 ml), tetramethylammonium chloride (2.30 g in 20 ml), and 11.73 ml of a solution containing cdc^{2-} ions following the method of Cotton and McCleverty.[3] The air-dried olive green product was used directly for preparing the dpi salt; yield 2.25 g.

Diphenyliodonium Bis(N-cyanodithiocarbimato)nickel(II), $(dpi)_2[Ni(cdc)_2]$ (I).—To a solution of 1 g of the above tetramethylammonium salt in 175 ml of water, a solution of 1.44 g of dpiCl in 100 ml of water was added with stirring. Both the solutions were at 50°. A yellowish green product separated immediately. After complete addition of the precipitant, maintaining the temperature, the stirring was continued for another 15 min. The product was collected by filtration and washed on the filter with water at 50°, followed once with methanol and finally with ether. The product was vacuum dried over P_4O_{10}; yield 1.90 g (98%). *Anal.* Calcd for $C_{28}H_{20}I_2N_4S_4Ni$: C, 39.4; H, 2.4; I, 29.8; N, 6.6; S, 15.0; Ni, 6.9. Found: C, 39.3; H, 2.3; I, 29.6; N, 6.7; S, 15.2; Ni, 7.1. The product decomposes to a brown residue at 120° and becomes black on continued heating. It is photosensitive and becomes brown gradually on exposure to light but is stable in the dark. It is soluble in methanol, acetone, chloroform, acetonitrile, nitromethane, py, DMF, and DMSO.

An acetone solution of the salt when treated with sodium iodide yields the relatively insoluble dpiI, confirming the presence of the diphenyliodonium ion.

Pyrolysis Reactions.—The diphenyliodonium salt (I, 2 g) was heated at 100–102° under reduced pressure in a drying pistol. The course of the reaction was monitored by intermittent weighing until the sample lost weight equivalent to about 2 mol of iodobenzene; this required 45 hr. At the end of this period a brown product, II, remained. The elemental analysis of a typical reaction product indicates that for every pair of sulfur atoms about one phenyl group is present. *Anal.* Calcd for $C_{16}H_{10}N_4S_4Ni$: C, 43.2; H, 2.3; N, 12.6; S, 28.8; Ni, 13.2. Found for II: C, 40.40, 40.7; H, 2.1, 2.5; N, 11.6, 13.0; S, 29.5, 27.0; Ni, 14.2. The electronic spectrum of this substance in a mineral oil mull showed peaks at 9250, 22,900 and 42,900 cm^{-1}.

The distillate was a pale yellow liquid occasionally containing a small amount of colorless solid. (The infrared spectrum of the liquid is superimposable on that of iodobenzene.) At other times only the colorless solid melting at 59° was obtained in the receiver. Where solid and liquid were both present in the distillate, the mixture was extracted with acetone and water was added to the solution until a faint cloudiness appeared. On cooling the mixture white needles melting at 59° separated. This was identified as phenyldithiobenzene.

When 8 g of $(dpi)_2[Ni(cdc)_2]$ was heated in four equal batches at 100–102° (5×10^{-2} mm) for 45 hr, 65 mg of phenyldithiobenzene was isolated.

Isolation of N-Cyanodiphenyldithiocarbimate (cddc).—A suspension of 1 g of II in 100 ml of acetone was boiled for 5 min and filtered hot. A large amount of brown residue was left on the filter. Water was added to the pale yellow filtrate until cloudiness appeared and the mixture was cooled to obtain white needles; yield 90 mg (16% on the basis that II is pure diarylated complex). *Anal.* Calcd for $C_{14}H_{10}N_2S_2$: C, 62.2; H, 3.7; N, 10.4; S, 23.7. Found: C, 62.4; H, 3.9; N, 10.1; S, 23.6. The compound melts at 121° to a pale yellow liquid and can be sublimed unchanged by heating at 100° (5×10^{-2} mm). It is stable at room temperature.

Timmons and Wittenbrook[6] have studied the chemistry of cyanodithiocarbimates and have characterized a number of aliphatic esters of this type. Our compound (cddc) has an infrared spectrum identical with those observed by these workers for compounds of the type $(RS)_2CNCN$, with the nitrile band at 2160 cm^{-1}, the C=N stretch at 1490 cm^{-1}, and the other characteristic bands at 1396 (vw), 1025 and 997 (both m), and 964 cm^{-1} (s). These are in addition to the expected monosubstituted phenyl bands.

Our identification of phenyldithiobenzene in the distillate from the pyrolysis reaction is expected. In their unsuccessful attempts to synthesize cddc Timmons and Wittenbrook obtained only phenyl sulfides. They reasoned that the ester was probably formed and decomposed under the reaction conditions.

Reaction of II with $(C_6H_5)_3P$. Isolation of $[Ni((C_6H_5)_3P)_2(cdc)]$ (III).—A methanolic solution of II (1 g in 100 ml) was added to an ethanolic solution of $(C_6H_5)_3P$ (1.18 g in 50 ml). After stirring for about 1 min, the mixture was filtered. The filtrate was stirred for 4 hr and the reddish brown product which separated was collected by filtration and washed with ethanol and hexane. The product was vacuum dried over P_4O_{10}; yield 0.30 g (19%). *Anal.* Calcd for $C_{38}H_{30}N_2P_2S_2Ni$: C, 65.3; H, 4.3; N, 4.0; S, 9.2. Found: C, 62.6; H, 4.2; N, 4.8; S, 9.7. Absorption bands in the infrared spectrum of this compound agree with those reported[3] for $Ni((C_6H_5)_3P)_2cdc$.

Physical Measurements.—Infrared spectra were recorded as mulls in mineral oil and in halocarbon or as liquid film between NaCl plates on a Perkin-Elmer 137 recording spectrophotometer, frequency being calibrated with polystyrene film.

Magnetic measurements were done by the Gouy technique using mercury(II) tetrathiocyanatocobaltate(II) as standard at 296°K. Product II is paramagnetic to the extent of 2.38 BM [$\chi_M = 2365 \times 10^{-6}$ cgsu; the molecular weight was calculated on the basis of the nickel analysis]; the observed magnetic moment is independent of field strength.

Analyses were run by Baron Consulting Co., Orange, Conn.

Results and Discussion

The diphenyliodonium ion has been used to precipitate the anionic bis(N-cyanodithiocarbimato)nickel(II) complex from aqueous solution. This salt is not unlike those previously reported. However, as we had anticipated, this salt is unique in that it undergoes self-arylation.

On heating *in vacuo* at 100° the salt I loses weight equivalent to 2 mol of iodobenzene. The product of this reaction, II, is impure and difficult to purify because of its low solubility. However, much can be learned about the course of the reaction from this substance.

Analysis of II shows it to approximate the expected composition, $Ni(S_2C_2N_2C_6H_5)_2$. The magnetic moment

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(5) F. M. Beringer, E. J. Geering, I. Kuntz, and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956).

(6) R. J. Timmons and L. S. Wittenbrook, *J. Org. Chem.*, **32**, 1566 (1967).

of 2.38 BM for II indicates a structural change to have occurred during the reaction. Cotton and Harris[7] have shown the anion of I to be planar. While our observed moment for II is too low for a pure octahedral compound, it is strongly suggestive of such an environment. This moment was calculated on the basis of the nickel analysis. A significant diamagnetic nickel impurity could be responsible for the low value, or the necessary polymeric structure (below) could give a nickel sulfide type of compound (presumably with a nickel–nickel interaction). Nickel sulfide is known to have a room temperature moment of about 2.5 BM.[8]

The isolation of diphenylated ligand, cddc, from II (although not in high yield) serves to indicate the site of arylation. This compound has been phenylated on both sulfur atoms; no evidence is available for nitrogen attack. Since cddc does not sublime out of the reaction mixture, under conditions where the free compound is known to be sublimable, we conclude it to be coordinated to the nickel. Apparently arylation takes place on a coordinated sulfur, and in the absence of a donor solvent no displacement occurs. When II is extracted with acetone, solution occurs, displacing arylated ligand; then cddc is removed from the complex and can be isolated.

Substance II also contains unarylated cdc. This is demonstrated by the isolation of the known compound Ni(cdc)$((C_6H_5)_3P)_2$ from a solution of II on the addition of triphenylphosphine.

These facts lead us to conclude that II has a polymeric, octahedral structure, with both cdc and cddc coordinated to the nickel(II).

If both sulfur atoms of the cdc are shared between two nickels, a rigid polymeric octahedral structure would result. Such sharing of sulfurs is well documented, and in this fashion a coordination number of 6 is easily attained. It is not at all surprising that the configuration about the nickel ion changes on arylation. The lowered ligand field exerted by phenylated ligand is insufficient to maintain a planar configuration.

The electronic spectrum of II (solid in mineral oil mull) contains a weak band at 9250 cm^{-1}. It is reasonable to assign this as the $^3A_{2g} \rightarrow {}^3T_{2g}$, defining $10Dq$ for the complex. This would support our assumption of a greatly reduced field for the arylated complex. We feel the other spectral features to be non d–d transitions because of their much greater intensity; thus, we cannot check the correctness of this assignment by comparison with other band positions.

There are two factors which could contribute to the diphenylation of the cdc. The first is the packing of ions in the crystal lattice of I. If the packing were such that the cdc ligands are not equidistant from the dpi ions, then attack on one cdc only could be favored. This seems unlikely.

The other factor is that proposed by Schrauzer and Rabinowitz[9] in the alkylation of bis(*cis*-ethylenedithiolates) of nickel(II), palladium(II), and platinum(II). They also observed alkylation to occur exclusively on one ligand and reasoned that after the first step the negative charge on the monoalkylated ligand becomes more localized. The most nucleophilic sulfur is then the remaining sulfur on monoalkylated ligand. A similar phenomenon is probably occurring in the phenylation of I, monophenylation causing a localization of charge on the nonarylated sulfur of the same ligand. Schrauzer and Rabinowitz found no evidence of an isolable monoalkylated species, quite consistent with this hypothesis. We, also, find no conclusive evidence for such a substance.

Acknowledgment.—We are grateful to the National Institutes of Health for support of this work under Grant GM 14080.

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[7] F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **7**, 2140 (1968).

[8] I. Tsubokawa, *J. Phys. Soc. Japan*, **13**, 1432 (1958).

[9] G. N. Schrauzer and H. N. Rabinowitz, *J. Am. Chem. Soc.*, **90**, 4297 (1968).